FIG. 5. Water sorption isotherms for freeze-dried lactose at (O) 14 and (●) 34 C.

FIG. 7. Variation in calculated isosteric heat with coverage for second adsorption cycle on spray-dried skimmilk powder.

isosteric heat of adsorption for water vapor on whole milk powder are given as a function of surface coverage in Figure 6. The q_{ST} values were obtained upon application of the Clausius-Clapeyron equation to the multitemperature adsorption data of Figure 1. The differential form of the equation:

$$(\partial \ln P / \partial T)_{n_s} = q_{ST}/RT^2$$

was used and values of q_{ST} were computed from the slopes of the straight lines obtained on plotting log P against 1/T at isosteric points of constant molar adsorption, n_s.

The internal energy curve, Figure 6, indicates that at low surface coverage, represented as moles of water absorbed, the heat of adsorption is high, 16 kcal/mole and decreases rapidly at increasing adsorption to a low value of approximately 8.5 kcal/mole. At further increased coverage the q_{ST} value again increases, reaching a value of approximately 10.7 kcal/mole. The shape of this curve di-

rectly reflects the observed temperature effects in the experimental adsorption isotherms (Fig. 1). The higher energy of adsorption at low coverage corresponds to the initial gas-surface interaction at low relative pressure, where the normal inverse temperature-adsorption relation was observed. The point where the heat curve crosses the heat of liquefaction of water, ΔH_L, corresponds to the intersection of all three isotherms at $P/P_o = 0.2$. The region where $q_{ST} < \Delta H_L$ corresponds to the segment of the isotherms where the positive effect of temperature on adsorption was observed. After the breakpoint in the sorption isotherm, where adsorption on amorphous lactose is no longer involved, a normal heat value of q_{ST} slightly greater than ΔH_L was observed.

The internal energy curve in Figure 6 is shown for the data obtained with the whole milk powder only; however, similarly shaped curves were also obtained for the skimmilk powders. Calculation of q_{ST} from the second adsorption isotherms at 14 and 34 C on spray-dried skimmilk yielded the different type of energy curve of Figure 7. This curve is typical of physical adsorption in general, with a high heat of adsorption at low coverage due to the initial water vapor solid surface interaction. The heat value steadily decreases as the volume adsorbed increases and the forces due to the solid surface fall off with distance, resulting in q_{ST} approaching ΔH_L asymptotically. Thus, when adsorption takes place on milk powder during the second cycle, when lactose is already in the crystalline form, a normal situation of decreasing adsorption on increasing temperature with an accompanying normal energy diagram is observed. Comparison of the data in Figures 2 and 3 for the
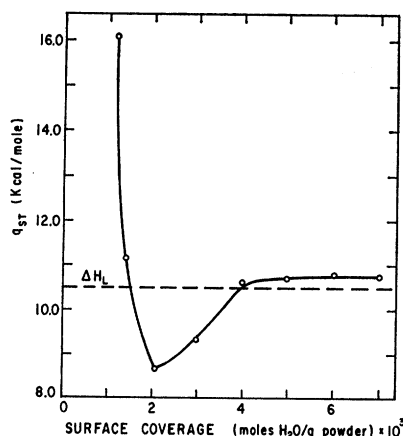

FIG. 6. Difference in the internal energy, per mole. The variation in the isosteric heat with increasing coverage for water adsorption on foam-spray-dried whole milk powder (ΔH_L = heat of liquefaction of water).
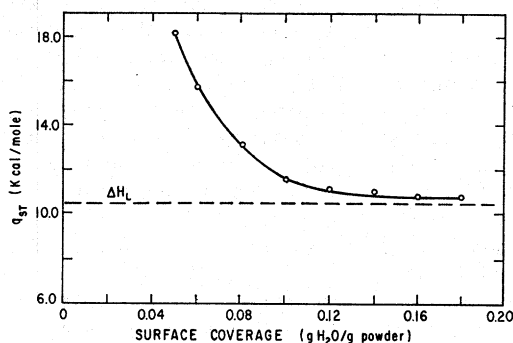
second adsorption isotherm clearly demonstrates this point.

Calculation of the heat of adsorption for water vapor on freeze-dried lactose, using the data of this paper for 14 and 34 C together with previous data (2) for 24 C, was not feasible as nonlinear graphs were obtained due to the nonequilibrium situation in adsorption on lactose and the occurrence of a phase change in the formation of the α-monohydrate from the glass. Using the data after the breakpoint at very high humidity, a value of $q_{ST} = 11.5$ kcal/mole was obtained. This must correspond to the binding of the hydrate water as the final amount of bound water at a relative pressure of 0.95 to 0.98 corresponds closely to the theoretical 5% moisture content of α-lactose-monohydrate. A value of $12.05 \pm .5$ kcal/mole was obtained calorimetrically for the heat of vaporization of the water bound by α-lactose monohydrate (4).

The mechanism of water sorption by dehydrated milk powders has been shown (2) to involve casein initially, at low relative pressure, but as the pressure increases toward 0.5 P_o the lactose glass becomes the principal water-binding site. After conversion of the glass to the crystalline form, moisture is released, and at $P/P_o > 0.5$ the salts rapidly absorb water. Finally, at higher relative pressures, water sorption on a swollen protein system is involved (3). The energetics of the water sorption process as depicted in the internal energy curve of Figure 6 are fully compatible with this mechanism. The initial high heat of adsorption, 16 kcal/mole, corresponds to the first water-protein interaction. The dip in the q_{ST} values may be attributed to surface mobility of sorbed water molecules leading to solubilization of the lactose, followed by crystallization. The low point on the curve probably indicates that the energy involved is the algebraic sum of the exothermic heat of adsorption and the endothermic heat of solution. This is in keeping with the changes in the position on the relative pressure scale of the breakpoints as the temperature is varied. Although the breakpoints occur at lower P/P_o values on increasing the temperature, the pressure values, P, increase with increasing temperature. When Clausius-Clapeyron type plots are made of log P against 1/T where P corresponds to the breakpoint pressure at the temperature, T, linear plots were obtained whose slopes yielded a value of 8 kcal/mole, close to the low point on the energy curve of Figure 6. Finally, after the breakpoint in the isotherm, the heat curve (Fig. 6) rises to a value slightly greater than ΔH_L, similar to that obtained in a second cycle on milk powder or for adsorption in general.

Thus, the suggested mechanism for water sorption is fully compatible with the thermodynamic evidence.

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Effect of Temperature on Water Vapor Sorption by Dried Milk Powders

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Abstract

The influence of temperature on the equilibrium water vapor sorption values for dried milk powders varied with the relative pressure P/P_o, in the temperature range between 14 and 34 C, with both positive and negative temperature effects on adsorption observed. Thermodynamic treatment of the data indicate an initial high isosteric heat of adsorption, q_{ST}, for protein-water binding, followed by lower energy values, less than ΔH_L, the heat of liquefaction of water, which are attributable to mobility of sorbed water molecules and solubilization and crystallization of lactose. The lactose crystallization-induced breakpoint in the isotherm occurred at lower P/P_o on elevating the temperature. In materials containing no amorphous lactose, only negative effects of temperature were observed with $q_{ST} > \Delta H_L$.

The lack of storage stability of dried milk products in warm humid environments is well known. In seeking means to avoid the deleterious changes which occur in powders under such conditions, we have studied the fundamental nature of the water sorption process itself (1, 2). In the present communication, we are reporting results of sorption measurements at three different temperatures near ambient.

These data on the extent of water binding at different temperatures are important, because the reactions leading to the adverse effects of moisture sorption on milk powder stability are catalyzed at elevated temperatures. Most importantly, the data at the several temperatures may be used to compute the isosteric heat of adsorption, which is a differential molar heat quantity defined by application of the Clausius-Clapeyron equation under the restriction that n_s, the number of moles adsorbed, be held constant. Such thermodynamic calculations yield information on the energetics of the sorption process which allows for its mechanistic interpretation.

Materials and Methods

Sorption studies were conducted on foam-spray-dried whole milk (5) and spray-dried skimmilk powders made in the Dairy Products Laboratory pilot plant. Freeze-dried skimmilk and lactose were also used as sorbents.

Water vapor sorption was determined gravimetrically at 14, 24 and 34 C, using the Cahn RG [2] recording electrobalance incorporated into a glass adsorption apparatus equipped with suitable accessories for outgassing the powders and controlling and monitoring temperature and water vapor pressure. The apparatus and experimental technique have been described in detail (1).

Extensive measurements of both sorption and desorption phenomena were made to determine the reversibility of the process.

Results

Water sorption data for foam-spray-dried whole milk powder at 14 and 34 C are shown in Figure 1, together with previously published data for 24 C (1). The data are presented as a function of relative pressure, P/P_o, where P is the pressure in the system and P_o is the vapor pressure of water at the temperature at which the sorption is measured. At pressures below 0.2 P_o there is a normal inverse relationship between the moles of water sorbed and the temperature; however, between $P/P_o = 0.2$ and the breakpoints in the isotherms there is a positive temperature coefficient of adsorption. Beyond the breakpoints, little temperature dependence is observed.

The temperature also affects the location on the isotherms of the breakpoint caused by lactose crystallization. On elevating the temperature the breakpoint occurs at a lower relative pressure. Similar thermal effects were ob-

[2] Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.
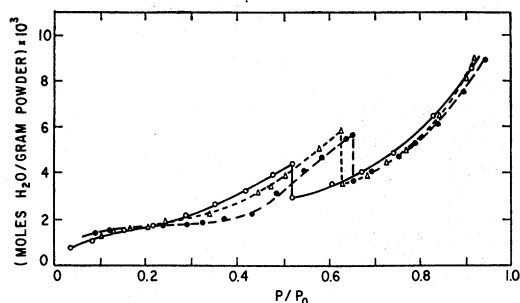
FIG. 1. Water vapor adsorption isotherms for foam-spray-dried whole milk at (●) 14, (△) 24, and (○) 34 C.

served with all sorbents containing amorphous lactose.

Data for two successive adsorption desorption cycles on spray-dried skimmilk powders at 14 and 34 C are shown in Figures 2 and 3, respectively. Hysteresis was observed on desorption in all cases, with the most pronounced loop in the first sorption-desorption cycle at 14 C. At both temperatures the extent of hysteresis was reduced in the second cycle, particularly at 14 C. The first and second desorption legs were coincident at both temperatures, whereas the adsorption legs differed in the two cycles at both temperatures. These data point to differences in the sorption processes in the two cycles.

Multitemperature sorption data for lyophilized skimmilks and for lyophilized lactose are given in Figures 4 and 5, respectively.

Discussion

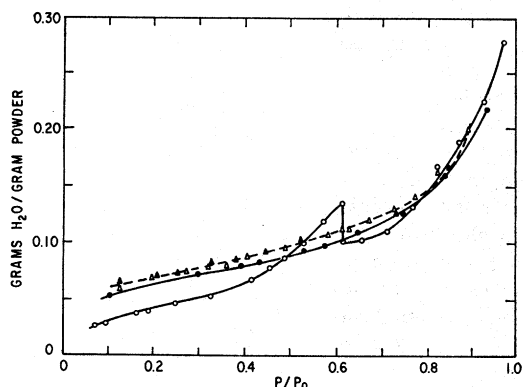The curious phenomenon shown in the adsorption isotherms for foam-spray-dried whole

FIG. 2. Water sorption isotherms for spray-dried skimmilk powder at 14 C. ○, adsorption (first cycle); △, desorption (first cycle); ●, adsorption (second cycle); ▲, desorption (second cycle).
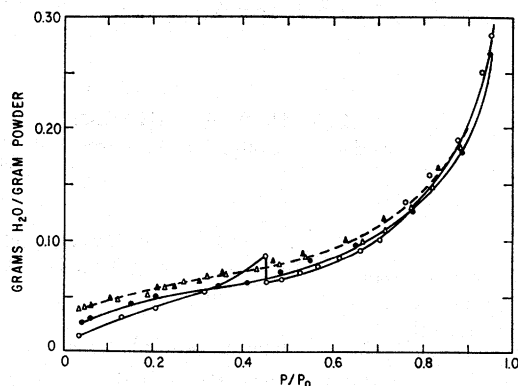

FIG. 3. Water sorption isotherms for spray-dried skimmilk powder at 34 C. ○, adsorption (first cycle); △, desorption (first cycle); ●, adsorption (second cycle); ▲, desorption (second cycle).

milk (Fig. 1) of increasing amounts adsorbed with increasing temperature leads to a set of thermodynamic properties consistent with a published (2) mechanism of water vapor sorption involving the various milk components.

Though not common, isotherms with such a positive temperature dependence have been reported previously (6, 7), and their thermodynamic implications have been discussed at length (7). Zettlemoyer (7) has pointed out that for such isotherms the isosteric heat of absorption, q_{ST}, is less than the heat of liquefaction, ΔH_L; the entropy of the adsorbed phase is high; and that both the low energy and high entropy values indicate high mobility of the adsorbed molecules.

Thermodynamic treatment of our data for sorption on milk powder yields results consistent with these properties. Values for the
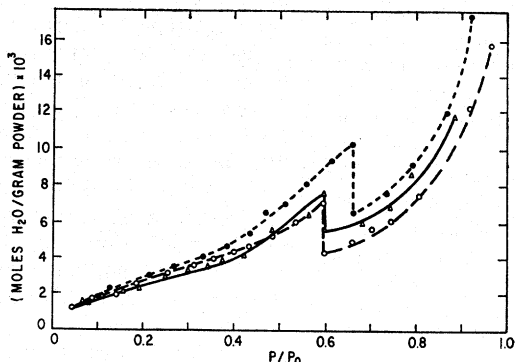

FIG. 4. Water vapor adsorption isotherms for freeze-dried skimmilk at (●) 14, (△) 24, (○) 34 C.